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APPLICATIONS OF MICROWAVE INDUCED CATALYSIS TO SOME ENVIRONMENTAL PROBLEMS: REDUCTION OF SO_2 AND NO_x AND DEHALOGENATION OF HYDROCARBONS

RAC PROJECT #400G

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ABSTRACT

The development of the concept of microwave induced catalysis as a method for promoting the rapid and selective reactions has been ongoing in this laboratory for a number of years. This project marks the first attempts to examine the feasibility and appropriateness of the concept for the decomposition or removal of several airborne environmental contaminants. These have included the decomposition of SO_2 and NO_x, the dehalogenation of several model aromatic and aliphatic hydrocarbons, and a brief look at decompositions of some aromatic hydrocarbons. In addition some experiments extending the research to the conversion of CO_2 possibly to alkane or alcohol products are currently underway. During the course of the research our understanding of the effects of microwave interactions with complex heterogeneous materials as they apply to these reaction systems has been substantially increased. This has allowed many advances in the design of an appropriate microwave reactor for the performance of the reactions as well as a much better feel for methods for optimization of reaction parameters.

PUBLICATIONS ARISING FROM THIS PROJECT

1. High Power Pulsed Microwave Catalytic Processes: A New Approach to Hydrocarbon Oxidation and Sulfur Reduction, M. Catherine Depew, M. Yat Tse, Haldor Husby and Jeffrey K. S. Wan, 11th Canadian Symposium on Catalysis, Halifax, July 1990, pp. 168-177.

2. Applications of High Power Microwave Catalysis in Chemistry, M. Yat Tse, M. Catherine Depew and Jeffrey K. S. Wan, Res. Chem. Intermed., 13(1990)221-236.

3. A Mechanistic Study of the Microwave Induced Catalytic Decompositions of Organic Halides, T. R. J. Dineson, M. Y. Tse, M. C. Depew and J. K. S. Wan, Res. Chem. Intermed., 15(1991)113-127.

INTRODUCTION

Although the potential of microwave power has been utilized in a variety of different engineering applications especially in radar and in the communications field as well as in heating and curing different materials, the concept of its use as an energy source for chemical reactions has only recently been appreciated. Part of the reason for this has been the bias of chemists, raised on the principles of quantum mechanics, who concluded that the energy provided by microwave irradiation was too low to cause sufficient excitation for bond breaking or transfer of electrons.

This work examines the application of a novel technology, now termed microwave induced catalysis to some of the problems still very significant in environmental pollution. This technology has been pioneered by Professor J. K. S. Wan at Queen's University and has found successful application to many industrial processes including the hydrodesulfurization of hydrocracked pitch [1], the synthesis of ethylene and higher hydrocarbons from methane [2,3], the water gas shift reaction [4], and the oxidation of hydrocarbons to alcohols [5].

The basis of this technology is the selective absorption of microwave energy and the resultant rapid surface heating of certain catalysts containing amorphous paramagnetic metals with very little energy absorption by either reagents or the catalyst support. Although most organic compounds do not efficiently absorb low frequency microwave radiation, it is possible to use a strongly absorbing sensitizer to concentrate and transfer the energy provided by the microwave source to the desired reagents. Microwave heating characteristics of some elements and compounds are shown in Table I; nickel, iron and cobalt are among the metals that have been widely used in microwave induced catalysis.

Table I
Effect of microwave heating on the temperature of certain elements and compounds [6].

Chemical	Temperature (°C)	Time (min.)
Co	1283	1
Co_2O_3	697	3
Cu	228	7
Fe	768	7
Fe_3O_4	1258	3
MnO_2	1287	6
Ni	384	1
NiO	1305	6
Zn	581	3

Microwave induced catalysis differs in several ways from conventional catalytic

methods; these differences offer distinct advantages in application to certain types of reactions. Firstly, the catalyst may serve a dual purpose both as a promoter of the chemical reactions on the surface and also as an efficient converter of the incident microwave to thermal energy necessary for the reaction activation energy. It is the selectivity of microwave interaction with different materials which enables the focusing of the energy primarily on the surface catalyst sites, precisely where reagent adsorption and reaction occurs, which optimizes this effect. In addition, the fact that the incident microwave energy can be switched on and off extremely rapidly, combined with the almost instantaneous heating that occurs in lossy materials upon absorption of microwave radiation, allows a high degree of control of reaction conditions including the catalyst surface temperature. As a result reactions can be initiated at catalyst surfaces even though the bulk of the reactor and reagents are maintained at or near ambient temperatures and pressures - in contrast, many conventional catalytic processes, especially those involving free radical intermediates such as hydrogen atoms, hydroxyl or organic radicals, often require elevated temperatures and pressures to induce the reactions. These requirements are not only costly but also may limit the maximum efficiency attainable for the process and favour unwanted side reactions.

Thus, experimental design has revolved around systems using pulsed microwave energy since these have proved to be the most efficient in reactions using metal powder [3] or supported metal catalysts [5]. During the on-cycle the microwave pulses supply the required energy for the catalyst surface to reach the activation temperature. While during the off-cycle, between each pulse packet, the metal and its support would conduct the heat away from the hot active sites and thus reduce their surface temperature. This cooling step can facilitate the desorption of the newly formed products and adsorption of the reactants on the sites. The actual rate of increase in temperature required to reach the activation temperature depends on several factors: these include the nature and configuration of the catalyst surface, the peak power of each microwave pulse, and the duration and average energy of the pulse packet. By carefully regulating the above mentioned parameters, desired reaction conditions can be easily achieved. An additional advantage of this technology is its flexibility - changes in the reactor design and parameters are relatively easy to accomplish allowing the tailoring of experimental conditions to suit the specific requirements of the gaseous, liquid or solid reagents or products under study.

The specific applications described in this report are the microwave induced decompositions of the acidic gases sulfur dioxide and nitric oxide, the dehalogenation of several model aliphatic and aromatic halohydrocarbons, and briefly the decomposition of some higher aromatic hydrocarbons. In the experiments with sulfur dioxide and nitric oxide the primary goal was to obtain reduction of these compounds to substances relatively innocuous so as not to require further treatment or processing (or pose additional environmental problems). Thus the goal was to reduce sulfur dioxide to oxygen and if possible sulfur; for nitric oxide - nitrogen and oxygen were pursued.

Several model organic and aliphatic halogenated hydrocarbons were decomposed using this technique with nearly 100% efficiency. By using a combination of gc, mass spectrometry and electron spin resonance detection the intermediates in the decomposition processes were investigated. As a result the free radical nature of the reactions can be clearly demonstrated. Many of the non-halogenated byproducts are of economic or chemical value and could be recovered in the microwave processing.

Finally, the decomposition of a few model polycyclic aromatic and other

hydrocarbons has been briefly examined. Decomposition to volatile, low molecular hydrocarbon products can be achieved. Again many of these products are recoverable and have substantial economic value as synthetic feedstock reagents.

EXPERIMENTAL DESIGN

Methods and procedures in microwave catalysis have been continuously evolving and at the present time there appears no general apparatus suitable for all applications. The optimal and proper apparatus has to be designed for each of the chemical systems to be investigated. However, with time and experience we have achieved a reasonable appreciation of many of the significant factors that influence chemical outcomes in the microwave processes, and have modified and designed the reactors to take advantage of these effects. One of the advantages offered by the microwave technology is its ready adaptability to a variety of different reagents and chemical systems.

Two basic types of reactor have been used for the work described in this project. Early experiments to demonstrate the viability of the technique and to test some of the basis ideas governing the use of microwave power in such systems were illustrated using a modified 400 W commercial microwave oven, i.e. a multimode cavity. The ovens were modified to contain a pyrex reactor connected to a vacuum line for injection of gaseous reagents; and provided with on-line gc analysis. The pyrex reactor containing a fixed bed of the catalyst material was suspended in the middle of the oven. A home-built pulse controller was used to program the on/off microwave power cycles. Typical conditions in this system used on/off microwave cycles of 2-10s/20-60s. The schematic diagram for such an experimental set-up is shown in Figure 1. While such a set-up is convenient for obtaining

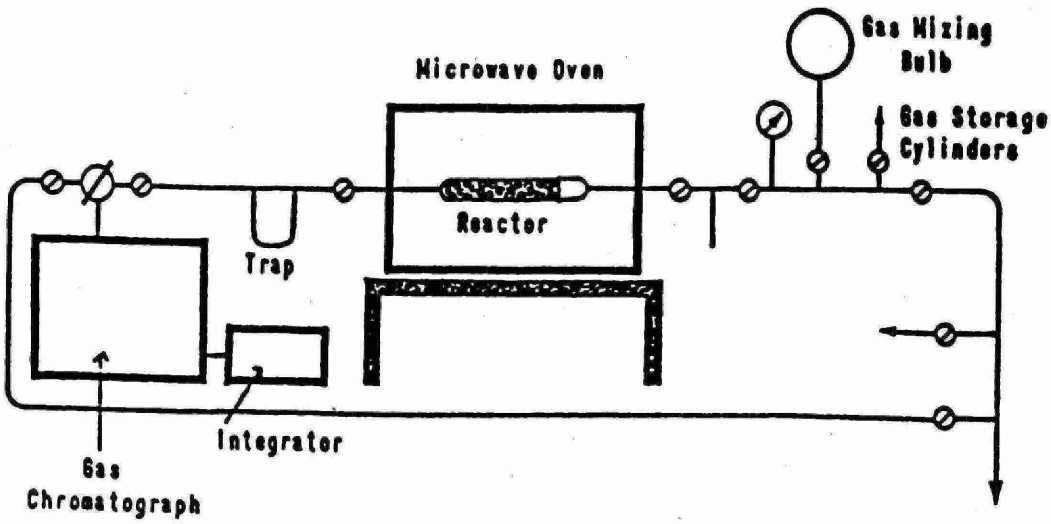


Figure 1. Schematic diagram of the multimode oven reactor.

qualitative results it is not ideal for obtaining accurate measurements regarding the energy input and efficiency of the system. In addition results from early experiments indicated that improved conversions and product selectivity and product selectivities could likely be better obtained using higher microwave power pulses for shorter durations.

Therefore, a moderately high power (Cober variable 3 kW, 2.45 GHz, Model S3F/4091) magnetron with pulse width gated for a few ms was incorporated into a reactor design. A Custom built pulse controller was used to control the period, duty cycle and power level in a reproducible manner. A circulator with a water cooled terminator served as an isolator to protect the microwave generator from reflected microwaves. A 20-db directional coupler in combination with a 30-db attenuator, a crystal detector and a Nicolet Explorer IIIA digital oscilloscope (model 204) were used to monitor the incident power amplitude and pulse width. A typical pattern of the microwave pulse shapes obtained is presented in Figure 2. Prior to experimentation the system was tuned so as to minimize the reflected microwave radiation; tuning was achieved by using a three-stub tuner and a tunable short. The measurements of the incident and reflected microwave power were taken using a cross-guide coupler, power meters (Hewlett-Packard 432A) and a Hitachi digital oscilloscope, model VC-6023.

It is advantageous to use waveguide sections for propagation of the power since loss is minimized, and an adapted waveguide section to enclose the actual chemical reactor for simplicity. Thus, microwaves from the magnetron were transmitted through a 7.2 x 3.4 cm rectangular S-band waveguide to the reaction cavity. The reaction cavity is essentially a 4 cm long section of waveguide with a pair of mica windows, transparent to the microwave

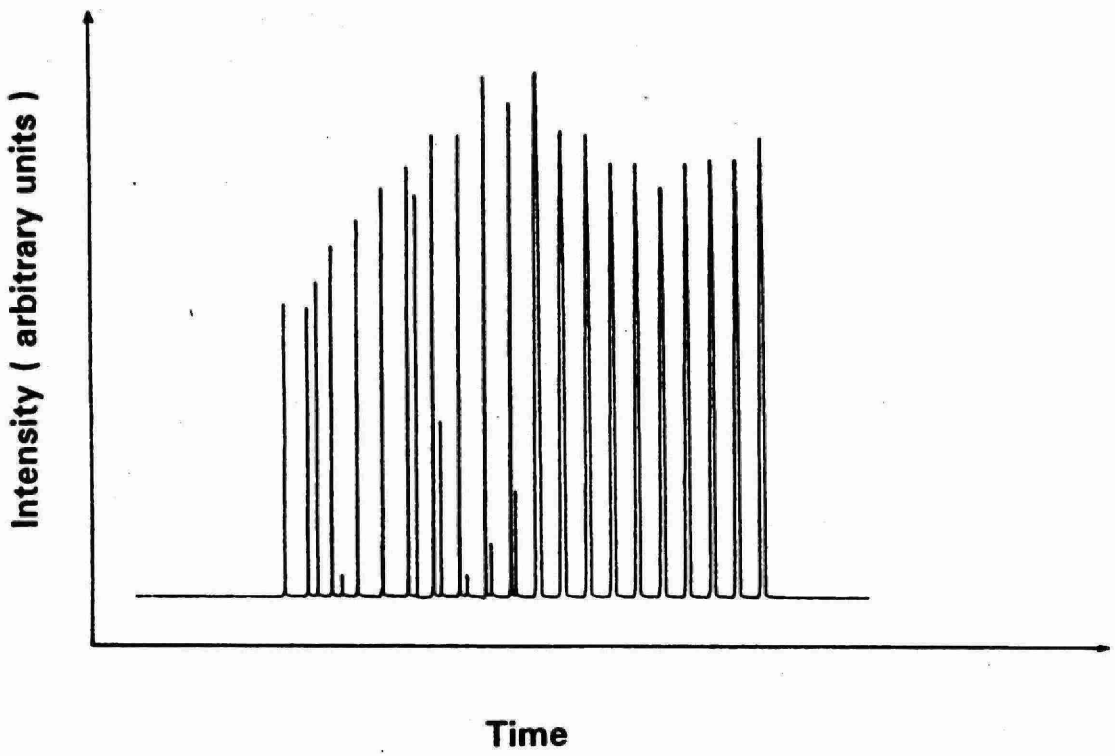
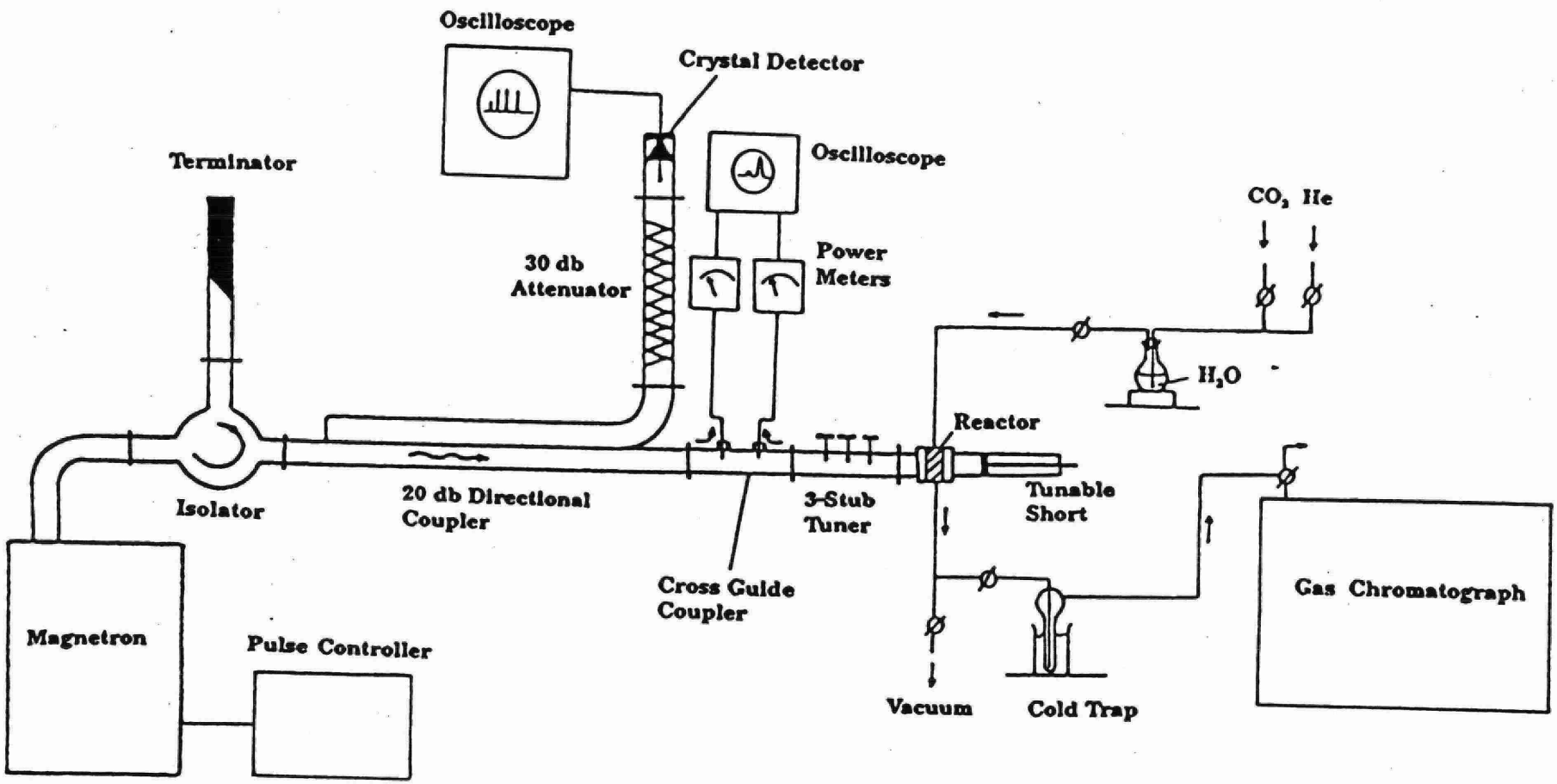


Figure 2. Microwave pulse shapes at an average power of 2.2 kW, period 8.3 ms.

Fig. 3 Waveguide Reactor in a Continuous Flow System



radiation, making an air tight seal. The catalyst was packed into a pyrex tube 7 cm long and 2 cm diameter (I.D.). The tube was then placed in the reaction cavity so that its long axis was perpendicular to both the direction of the microwave propagation and to the electric field so as to maximize exposure to the incident radiation. Reactants were introduced into the cavity via a drilled hole in the side wall of the cavity whereas the exit from the reactor was connected to the gas chromatograph via a cold trap. After a 20-30 min equilibration period, the catalyst was subjected to 168 ms pulses of microwave irradiation at 2.2 kW average power followed by 20 s rest period. The schematic diagram for this system is outlined in Figure 3.

Both the feed and product streams were analyzed by a Hewlett-Packard 5890A gas chromatograph with either thermal conductivity or flame ionization detectors as appropriate. Columns used for product separation include: J & W Scientific GS-Q fused silica column (0.63mm x 30m), Porapak Q or Porapak N, and Molecular Sieve 5A. The latter was pretreated for the NO_x experiments in order to prevent tailing. Product identification was achieved by comparing retention times with those of the appropriate standards. Quantitation of gas samples was preformed using a Hewlett Packard integrator (Model 3390A) and standard calibrated mixtures from Matheson Gas Products. Reagent gases were used as received from Matheson.

In the experiments with the halogenated organic reagents mixtures of 10% volatile short-chain alkyl halides in He were circulated at flow rates from 20-40 mL/min over an alumina supported iron oxide catalyst (SMR7-2946). Aryl halides were carried through the catalyst bed as saturated He solutions. Mass spectrometric analyses were carried out using a custom-modified Spectrum Scientific SM 1000M quadrupole mass spectrometer.

Several configurations and types of catalysts have been used in the study, including metal powders, wires, gauzes, as well as commercially available and custom synthesized supported catalysts having metal powders dispersed in a porous, non-lossy support. It has been found that optimum selection of the catalyst must take into consideration the nature of its chemical properties towards the chemical reagents and products as well as its interactions with the microwave radiation. Commercial catalysts used include Ni-1404, Ni-1600, Cu-1700, Cu-1132 and Ti-0404 from Harshaw/Filtrol Partnership, C-12 CO conversion catalysts from Chemetron-Girdler, C101-V_2O_5 from Catalyst and Chemicals, iron oxide on alumina (SMR7-2946) from Grace Chemical Co., and Ni, Fe, Cu, graphite and CuO powders, Ni and Fe mesh screening, and Ni wires. For some of the experiments initial activation of the catalysts under H_2 (30 kPa) while irradiation with 5 x 10s of 400 W average microwave power was performed to remove oxides from the catalyst surface.

RESULTS AND DISCUSSION

1. SO_2 EXPERIMENTS:

There are several fairly efficient technologies for the removal of SO_2 from flue gas emissions by further oxidation and neutralization of the acidic products [7 and references therein]; however, the highly corrosive oxidized products are expensive and unpleasant to

deal with and the neutralized residues also pose disposal problems. In this work our goal has been to design the catalyst and experimental conditions so as to decompose SO_2 reductively to O_2 and either sulfur or metal sulfide products. Many of the latter are desireable commercial commodities. Similarly the reductive decomposition of nitric oxide to N_2 and O_2 was the goal in part 2 of the research. A few of the results obtained will be summarized to illustrate the potential of microwave induced catalytic decomposition of these acid gases.

Typically 5% SO_2 in air was passed over a fixed catalyst bed of metal powders or commercially available supported catalysts. After study of a wide variety of catalysts it was found that those containing substantial amounts of Ni and/or nickel oxides performed well in the removal of SO_2 from the feed stream. Especially Harshaws Ni-1404 was found to heat rapidly in the microwave field, have sufficient surface area and chemisorption for efficient adsorption of SO_2, and cause reductive decomposition. Typically greater than 99% of the SO_2 could be removed from the reagent gas stream over this catalyst. In addition it was found that the catalyst could be reused for many experiments with only minor decrease in effectiveness; at this point regeneration of the catalyst by microwave irradiation under H_2 flow returned it to its original reactivity.

In order to verify that decomposition of the SO_2 was occurring, experiments using 100% SO_2 or SO_2 in He were carried out to show that substantial concentrations of O_2 were evolved during the irradiation (Figure 4). No O_2 was generated in any blank experiments, with or without microwave irradiation; however, on microwave irradiation of the catalysts saturated with SO_2 the reagent acid gas concentration fell dramatically and the production

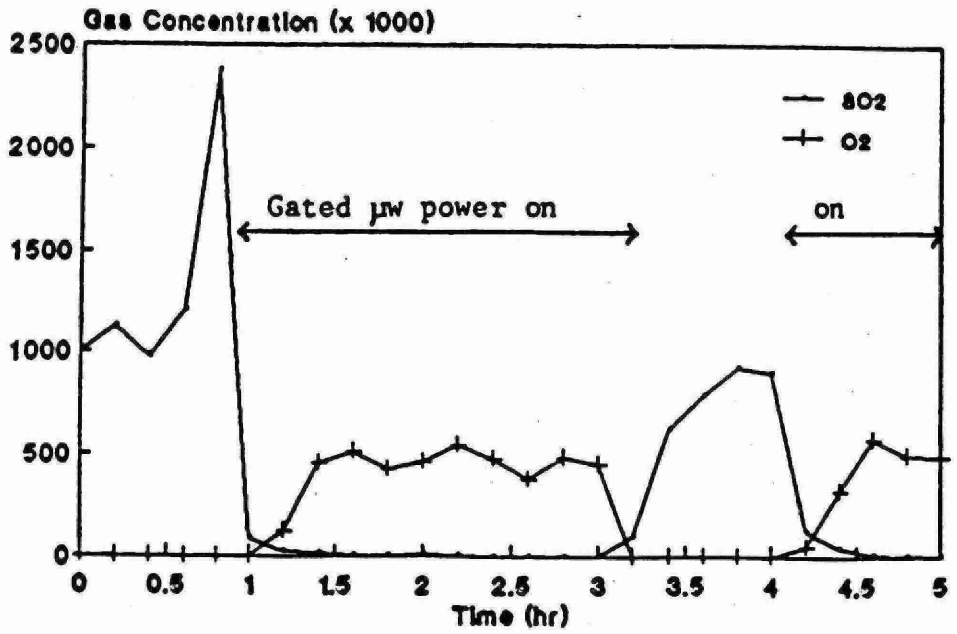


Figure 4. Decomposition of SO_2 over Ni/Nickel oxide catalyst (Harshaw Ni-1404).

of O_2 was simultaneously observed. Each time the microwave pulse train was interrupted the SO_2 concentration in the effluent reappeared; with irradiation it again decreased and oxygen was detected in the effluent stream. It is important to remember that the conditions of this experiment involve the continuous flow of 100% SO_2 after prior saturation of the catalyst with this reagent - the fact that the SO_2 levels are below the detection limits of the gc in the effluent gas stream are highly encouraging. The formation of some as yet incompletely characterized sulfur complex with the catalyst was indicated by the total S analysis of the spent catalyst as compared with the microwaved catalysts not exposed to SO_2. Similar results were obtained from the Harshaw Ni-1600 and Cu-1700 catalysts; the Ni-1600 catalyst, however, became easily poisoned and inactive on repeated use and could not be readily regenerated. Other catalysts which showed good heating responses to microwave irradiation but did not cause effective SO_2 reduction included Harshaw's V_2O_5 and Ti-0404 - these catalysts did not show the requisite chemisorption of SO_2 which appears necessary for high activity. Several experiments were also done using custom made catalyst pellets containing various amounts of graphite and Ni powders; microwave induced decompositions of SO_2 over such catalysts did occur with efficiencies of approximately 50% producing Ni sulfides and some sulfur. The lower efficiencies may be due to the lower porosities and surface areas of these catalysts compared to the commercial supported catalysts such as Ni-1404.

Experiments in which SO_2 was flowed over aqueous slurries of various powdered materials which strongly absorb microwave energy were also conducted. As shown in Table II, little or no reaction occurred over graphite, while quite substantial reductions in the SO_2 concentrations occurred over Ni and Fe powders (35 and 60% respectively). Oxygen was evolved during the irradiation and appreciable concentrations of sulfur were detected in the dried used catalysts. In contrast to these results reaction over Cu powder resulted in oxidation to $CuSO_4$; no O_2 evolution was detected. Although the removal of SO_2 was less than quantitative in these metal powder/H_2O experiemnts the contact of the reagent gas with the metal powder surface in the reactor is a significant limiting factor.

Table II.
Reaction of SO_2 over Aqueous Slurries of Metal Powder Catalysts.

Catalyst	% SO_2 Removed	Products
graphite	10	CO, CO_2, O_2
Ni	30 - 35	O_2, Ni_xS_y, S_x
Fe	60	O_2, Fe_xS_y, iron oxides, S_x
Cu	30	$CuSO_4$,

2. NO_x EXPERIMENTS:

Experiments using 25% NO in He over selected catalysts also indicated efficient decomposition of this gas under microwave irradiation. It was interesting that Cu-1700 and Cu-1132 which had shown good activity in the SO_2 experiments removed essentially none of the NO. However, Ni-1404, Ni-1600, custom Ni/graphite catalysts, and C-12 (an Fe_2O_3 containing catalyst) removed >99% of the NO introduced as shown in Figure 5. These catalysts were also found to be active for long periods of use and also could be readily regenerated several times. The products detected were N_2 and O_2, and also at prolonged reaction times some N_2O. In addition as the catalysts aged they did become oxidised and increasingly crumbly; such catalyst poisoning in the decomposition of NO is a relatively widespread problem [8]. In order to mitigate this problem experiments using reagent gas streams using 25% NO in He with the addition of 10% of either H_2, CO or CH_4 were reacted. This greatly prolonged the catalyst lifetime (by at least an order of magnitude) by reducing the amount of catalyst oxidation. No N_2O was detected in the H_2 or CH_4 experiments; however, both N_2O and CO_2 were produced along with the nitrogen and oxygen when CO was the coreagent gas added.

These results indicate the feasibility of adapting the microwave induced catalytic technology to the decomposition of NO, even in high concentrations. Much further work is needed to discover an optimum catalyst which combines the high degree of chemisorption needed with resistance to oxidation and ease of regeneration. Another asset that the microwave technology provides is the possibility of using several different catalyst beds in series to selectively decompose different pollutants.

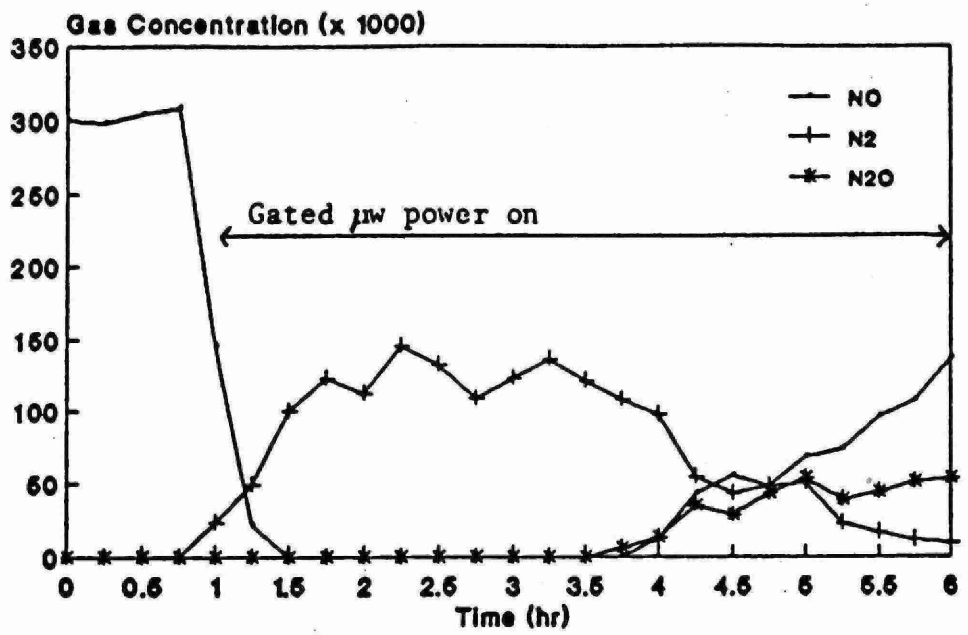


Figure 5. Decomposition of NO over Iron oxide catalyst (Girdler C-12). Microwave pulse conditions 2.5s on/30s off; flow rates 5-15 mL/min.

3. DEHALOGENATION OF ALIPHATIC AND AROMATIC HYDROCARBONS:

a. The decomposition of halogenated aliphatic compounds:

Chloromethane is the simplest model organohalide and has also been used in a previous study of decomposition by mercury sensitization [9]. In both of these microwave and photosensitization systems only the metal (Ni or Fe and Hg, respectively) absorbs the incident radiation, hence the common concept of sensitization. Both chemical systems essentially remove the chlorine from further chemical activity by formation of stable metal chlorides. However, experimentally these two systems are quite different; the Hg photosensitized decomposition is a homogeneous gas phase photochemical reaction, while the present microwave induced catalytic decomposition is mainly a primary surface reaction with the chlorobenzene initially chemisorbed at the metal sites of the catalyst surfaces.

Initiation of the breakdown of chloromethane begins with cleavage of the carbon-chlorine bond of the chemisorbed molecule during the transient microwave pulsed irradiation.

$$M/H_3C\text{-}X_{ads} \longrightarrow H_3C^{\cdot} + MX \qquad (X=Cl, Br) \tag{1}$$

Application of microwave pulses rapidly heats the metal sites of the catalytic surfaces to produce a very high, localized, transient temperature which leads to the selective breaking of the carbon-chlorine bond. The reactive methyl radical further undergoes rapid reactions with any available molecules either before or after its desorption from the surface.

$$H_3C^{\cdot} + 1/2H_2 \longrightarrow CH_4 \tag{2}$$

$$2CH_3^{\cdot} + H_2O \longrightarrow H_3COCH_3 + H_2O \tag{3}$$

In our reaction system the residual hydrogen from the activation of the alumina supported iron oxide catalyst is readily available to the methyl radicals resulting in the formation of methane. Adventitious water in the catalysts also reacted with the methyl radicals forming methanol and more methane. In all cases methane was the predominant product formed; only traces of ethane were detected indicating that the methyl radicals were relatively far apart on the catalyst surface. The small quantities of dimethyl ether detected are likely formed as a result of reactions such as the following:

$$2H_3COH \longrightarrow H_3COCH_3 + H_2O \tag{4}$$

The decomposition profile of chloromethane is shown in Figure 6; initial introduction of chloromethane into the reactor resulted in chemisorption on the cool catalyst surface. After saturation of the catalyst, gated microwave irradiation was commenced as indicated by the vertical line. The immediate sharp increase in the amount of chloromethane detected in the effluent gas is due to the non-equilibrated desorption as the catalyst surface rapidly is heated. This is a characteristic observation in the multimode microwave oven due to the fact that the magnetron power supply requires a substantial rise time before reaching operating power. Once the magnetron reaches peak efficiency a rapid decrease in the

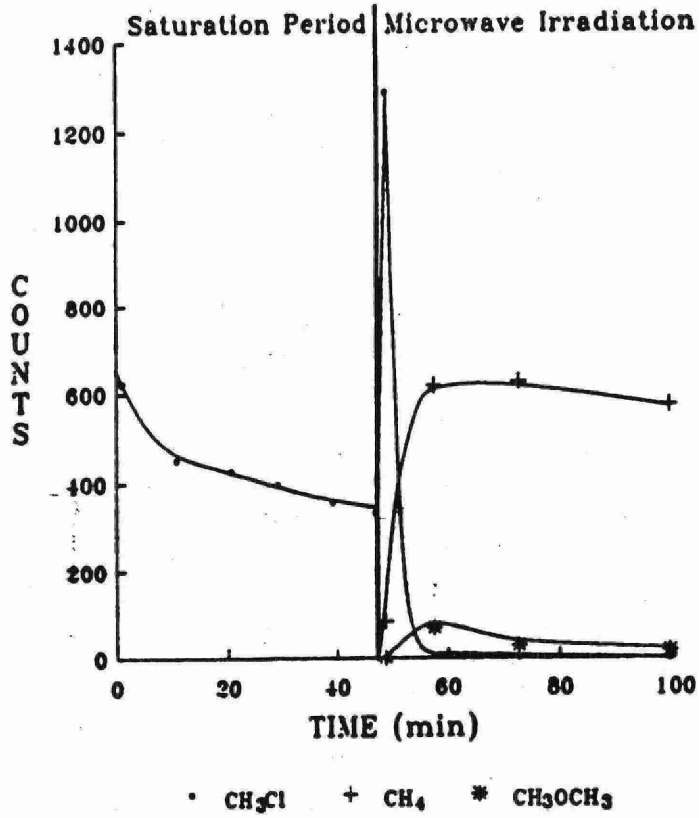


Figure 6. Decomposition of chloromethane in a circulating microwave oven reactor.

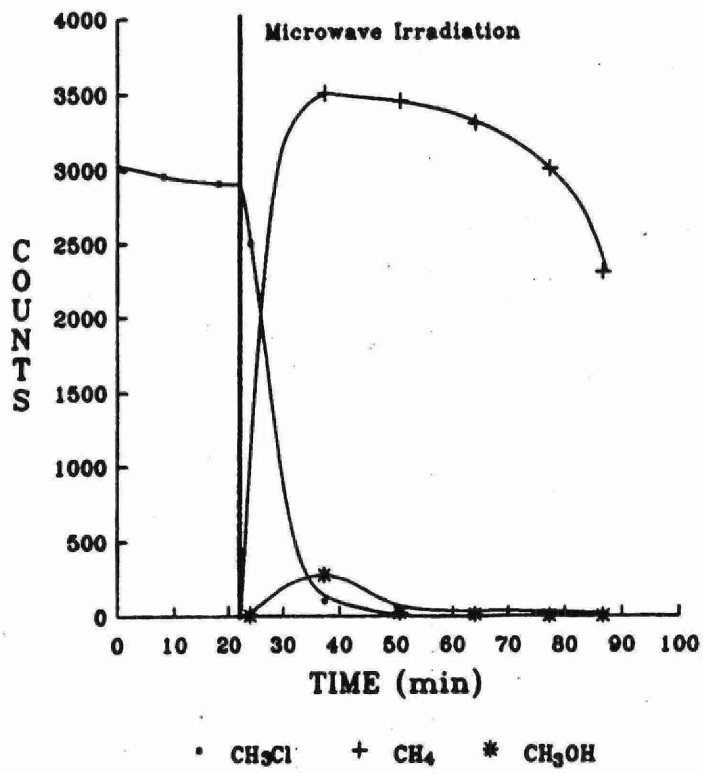


Figure 7. The decomposition of chloromethane in a circulating high-power waveguide reactor.

amount of chloromethane present was observed with a corresponding rise in the production of methane.

As can be seen in Figure 7, similar experiments using the 3 kW magnetron (which has a much faster power supply rise time) with shorter irradiation pulses avoids much of the desorption problem and increases reaction efficiency. For this experiment an average power of 2 kW was used with pulse duration 400 ms. Although methane is again the principal product in the higher power experiments, methanol instead of dimethyl ether is the principal oxygenated product formed. This is likely due to the different heating profiles of the catalyst surface in the two experiments; the more rapid temperature increase effected by the higher power system likely causes efficient cleavage of any adventitious water in the catalyst matrix to hydroxyl radicals resulting in the methanol formation.

The product profile observed for decomposition of bromomethane in the microwave multimode oven is shown in Figure 8. The lack of observed desorption of bromomethane at the start of the irradiation period may be explained by the effect of the weaker C-Br bond - apparently even the first few pulses before the oven reaches maximum power are sufficient to cleave this bond.

Figure 9 shows the decomposition of dichloromethane in the multimode oven; similarly to the chloromethane case the figure illustrates first adsorption onto the cool catalyst surface, desorption and some decomposition due to heating with a relatively weak field, and more rapid decomposition as the magnetron reaches peak power. It would be expected that if the chlorines were sequentially removed, the formation of chloromethane would first be observed, while cleavage of the second C-Cl bond would produce methane as in (5) and (6).

$$M/H_2CCl_2 + 1/2H_2 \longrightarrow H_3CCl + MCl \qquad (5)$$

$$M/H_3CCl + 1/2H_2 \longrightarrow CH_4 + MCl \qquad (6)$$

However, if the decomposition proceeds with the simultaneous removal of both chlorines an intermediate methylene radical would result with the accompanying formation of ethylene.

$$M/H_2CCl_2 \longrightarrow H_2C^{-} + MCl_2 \qquad (7)$$

$$2CH_2^{-} \longrightarrow C_2H_4 \qquad (8)$$

The observed products in the dichloromethane decomposition include chloromethane, methane, and ethylene. In the absence of clear experimental evidence to eliminate either of these mechanisms, we believe that most likely both mechanisms are operating simultaneously.

In order to establish that the hydrogen involved in the methane formation observed in reaction (2) is mainly the residual hydrogen left in the catalyst after activation, isotope labelling experiments were performed. Deuterium free H_3CCl was reacted over a D_2 activated catalyst and the products were analyzed by mass spectrometry. The presence of deuterated product confirmed that surface reactions were taking place at least to the extent that this isotope was incorporated into the organic products. The major product of

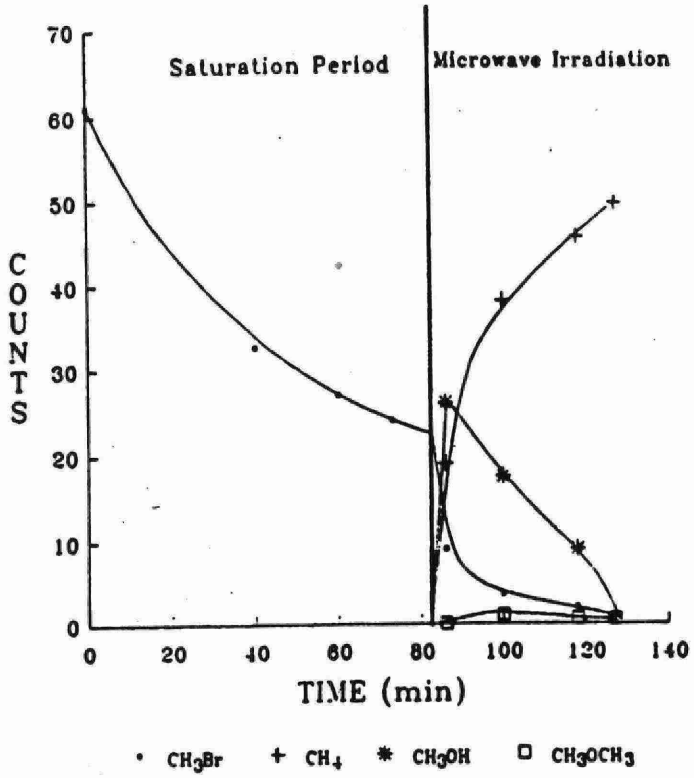


Figure 8. The decomposition of bromomethane in a circulating microwave oven reactor

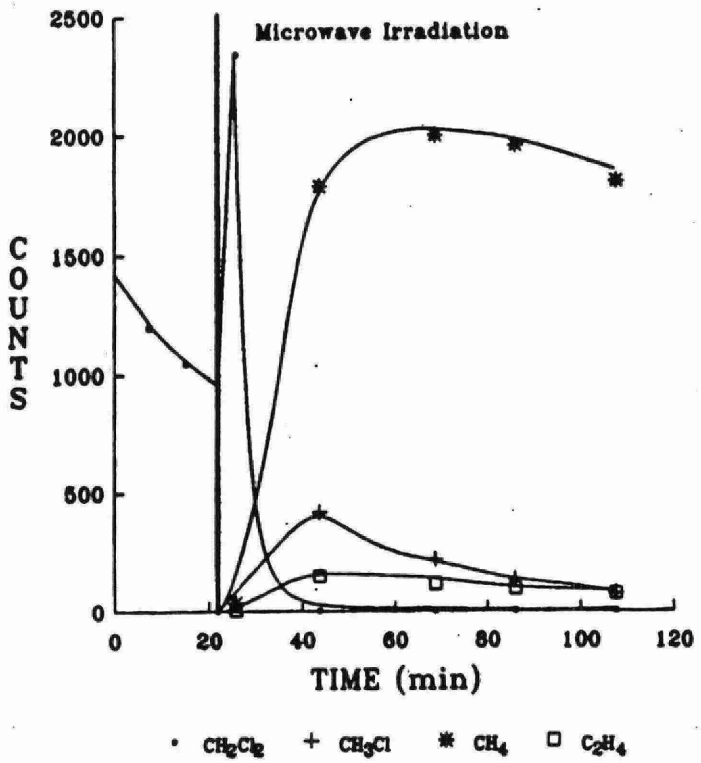


Figure 9. Decomposition of dichloromethane in a circulating microwave oven reactor.

chloromethane decomposition was expected to be partially deuterated methane.

$$H_3C^{\cdot} + 1/2\,D_2 \longrightarrow H_3CD \qquad (10)$$

The mass spectrometric results observed in the system in which the catalyst is activated with D_2 vs H_2 showed an increase in the intensity of the peaks at m/z = 15, 16 and 17 relative to those at 14, 15 and 16 consistent with the conclusion that most of the hydrogen in the products arises from this source. Further experiments using D_2O were also consistent with this conclusion.

b. The decomposition of aryl methyl halides

The direct esr detection of methyl or methylene radical intermediates in microwave processing of halogenated methane is extremely difficult due to the highly reactive nature of these intermediates and the strongly paramagnetic nature of the catalysts used. The use of spin traps to stabilize the radical intermediates for subsequent esr analysis is also not practical in our present reactor system, as the spin traps themselves will be subject to microwave induced decomposition. Nevertheless, it is a high priority in this laboratory to establish the free radical nature of these reactions by direct spectroscopic methods, including both fluorescence and esr. In order to approach this in the dehalogenation reactions, a specific model system to allow the direct observation of the primary organic radical intermediates was chosen. Thus, as it is known that the triphenylmethyl (trityl) radical is persistent for days in solution [10], reagents such as triphenylmethyl chloride and bromide were studied.

The intensity of the esr signal due to the trityl radical in solution was found to increase with the microwave processing time (Figure 10). This is the first direct experimental evidence of the primary organic radical intermediates being generated in the microwave induced reactions. Gas chromatographic analyses of the decomposition of powdered mixtures of triphenylmethyl chloride with Fe or Ni powders show the formation of benzene and chlorobenzene in a 6:1 ratio. The organic products can be accounted for by the following reactions.

$$M/(C_6H_5)_3CX \longrightarrow (C_6H_5)_3C^{\cdot} + MX \qquad (11)$$

$$M/(C_6H_5)_3CX \longrightarrow C_6H_5^{\cdot} + (C_6H_5)_2C^{\cdot} + MX \qquad (12)$$

$$C_6H_5^{\cdot} + 1/2H_2 \longrightarrow C_6H_6 \qquad (13)$$

$$C_6H_5^{\cdot} + (C_6H_5)_3CX \longrightarrow C_6H_5X + (C_6H_5)C^{\cdot} \qquad (14)$$

$$(C_6H_5)_2C^{\cdot} + H_2 \longrightarrow (C_6H_5)_2CH_2 \qquad (15)$$

$$2C_6H_5^{\cdot} + H_2O \longrightarrow C_6H_5OH + C_6H_6 \qquad (16)$$

The formation of benzyl alcohol in the presence of adventitious water may not proceed as outlined in (16), as the reaction may possible involve OH radicals as intermediates. Again it is not possible to detect the triplet methylene radicals in solution by esr but the confirmation of the trityl radical intermediacy and the accounting of all the major organic products, including diphenylmethane, clearly establishes the free radical mechanism of the primary processes in the microwave induced catalytic decomposition of organohalides.

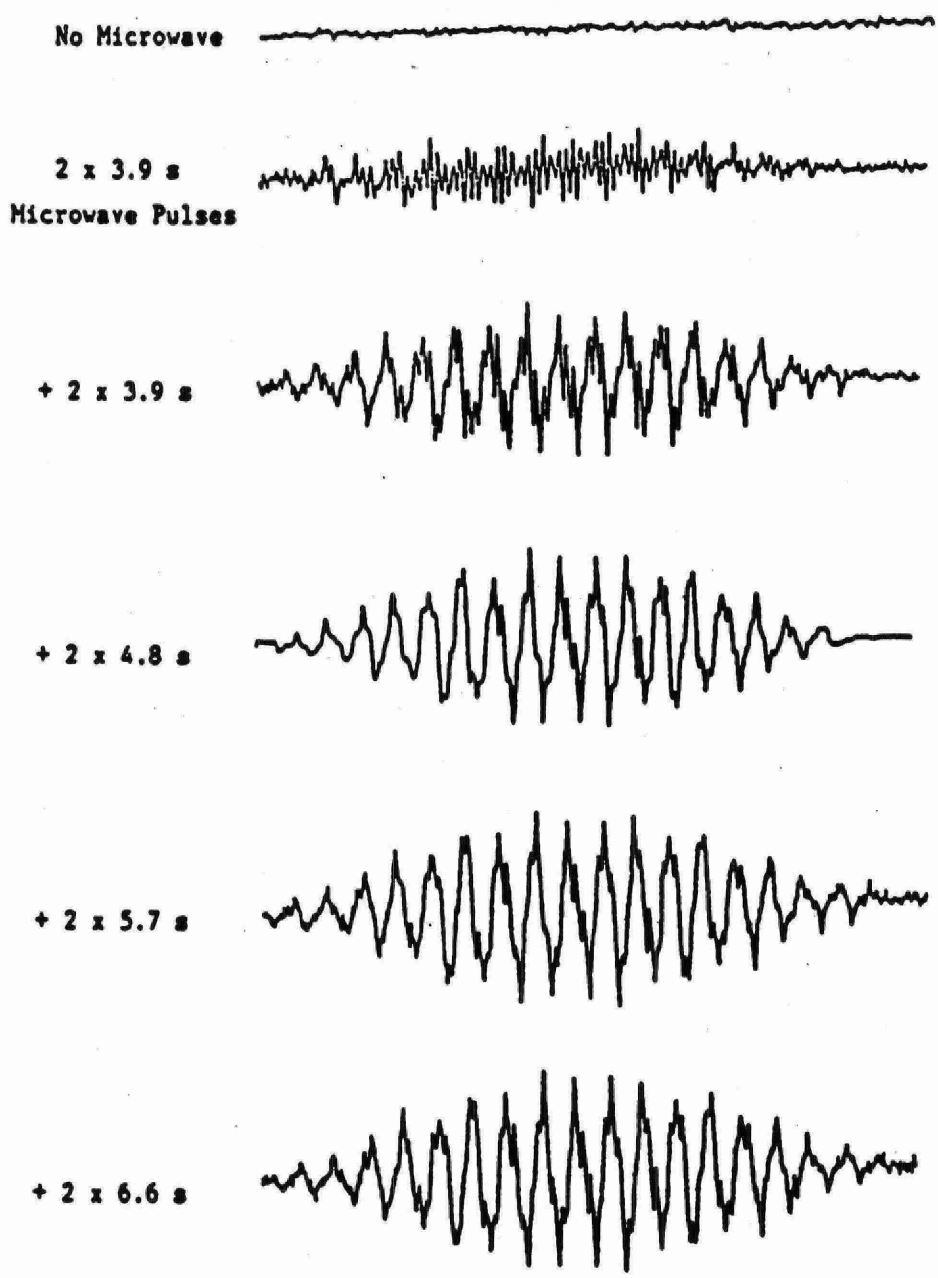


Figure 10. Esr observations of the trityl radicals produced as a function of increasing microwave energy (top to bottom).

c. The decomposition of aryl halides.

The removal of halogenated aromatics has received much environmental attention due to their toxicity and resistance to biodegradation which frequently results in their bioaccumulation at various stages in the food chain. Microwave catalytic decompositions of such aromatic halides can yield significant conversion to benzene, carbon dioxide, water and methane under a variety of experimental conditions. Harshaw Ni-1404 and Grace SMR7-2946 catalysts were used in this portion of the study; Figure 11 shows the decomposition of chlorobenzene over the iron oxide catalyst. The experiment was conducted in a circulating microwave oven reactor with the microwave pulse train (4s on/ 26s off) initiated after 45 min of equilibrating the catalyst surface with the chloride. After commencement of the irradiation an initial desorption of the chloride was noted followed by a decrease in this reagent concentration and an increase in the benzene production.

The Ni-1404 catalyst produced slightly different results; a typical experiment is shown in Figure 12. This experiment shows a single pass of He and chlorobenzene over the activated catalyst bed. The reagent was flowed over the catalyst initially until saturation occurred and the breakthrough of excess chlorobenzene was noted (0-110 min); a 3.9 s microwave pulse train reduced the chlorobenzene level to ~40% of the initial concentration with the concomitant production of benzene, water, carbon dioxide and methane. Using a longer pulse width of 6.9 s complete decomposition of the chlorobenzene occurred and in

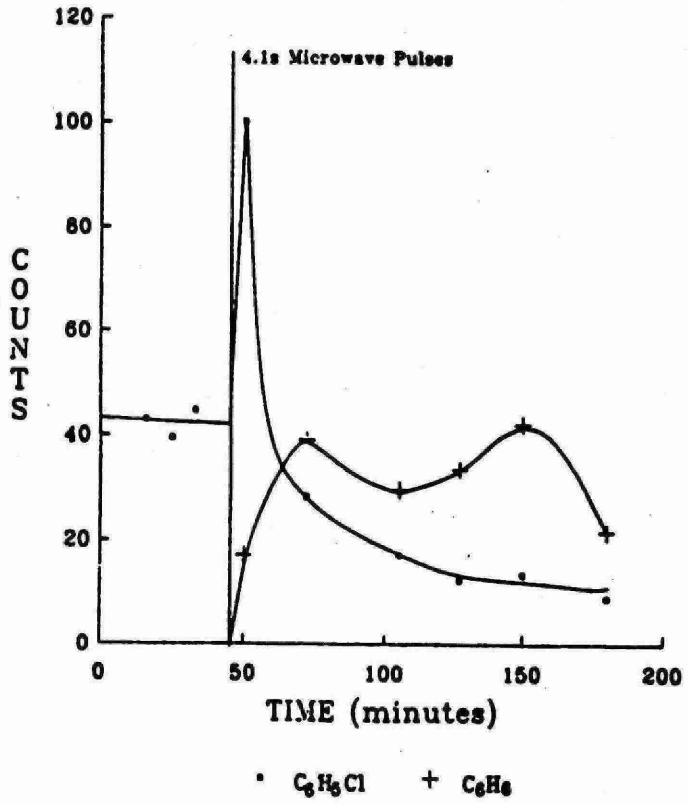


Figure 11. Decomposition of chlorobenzene in a circulating microwave oven reactor.

addition the benzene produced was also decomposed to C1 products and water. Total chloride analysis of the catalyst after reaction indicated the retention of the chloride on the catalyst surface; this was the general result for all the organohalide decomposition experiments.

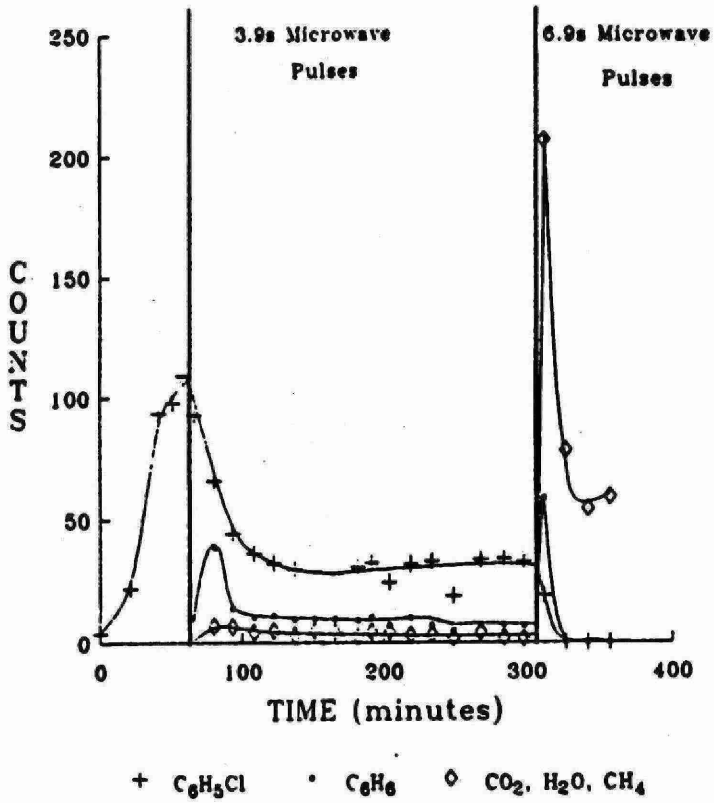


Figure 12. Decomposition of chlorobenzene in a flow-though microwave oven reactor.

4. Decomposition of Some Model Hydrocarbons:

Anthracene, ascorbyl palmitate, limonene, and n-butyl benzene were selected as representatives of several classes of aromatic and aliphatic hydrocarbon molecules. As can be seen from Figure 13 the decomposition of these compounds in a multimode oven over metal mesh catalysts or Harshaw Ni-1404 catalyst was quite readily achieved. The products detected were principally low molecular weight hydrocarbons such as ethylene, acetylene and ethane. Some methane was also no doubt produced but was not monitored in this particular set of experiments. No products eluting at retention times longer than those for C7 and C8 hydrocarbons could be detected, and products higher than C5 were in all cases minimal. These results as well as previous work involving the decomposition of oil sands materials, bitumens, and ashphaltenes [11] indicate that decomposition of complex polyaromatic hydrocarbon molecules is readily feasible using this technology.

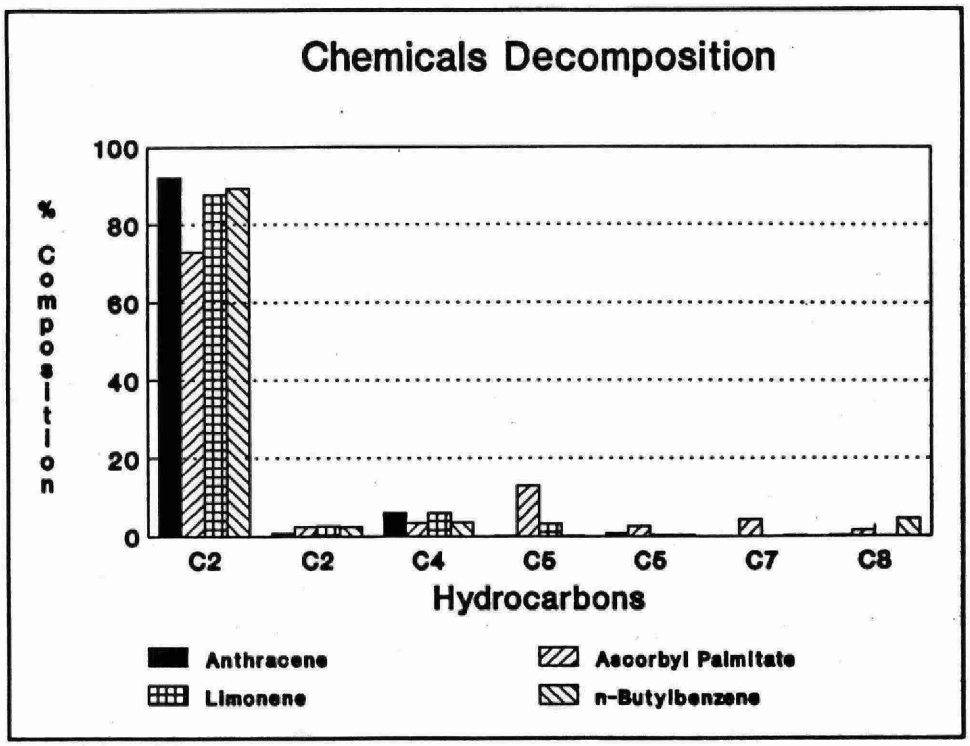


Figure 13. Relative hydrocarbon product distributions from microwave induced decompositions of several model chemical systems.

CONCLUSIONS

The technology of microwave induced catalytic decomposition has been demonstrated to be efficient and versatile towards decomposition of many organic and inorganic air pollutants. We believe that it is truly an enabling technology which has much greater potential for development in this area than has yet been demonstrated. The application of this technique to achieve the reduction of SO_2 and NO to oxygen and either metal sulfides or nitrogen is a novel approach to dealing with these acid gas pollutants which avoids production of more highly oxidised and possibly corrosive products. Dehalogenation of either singly or multiply halogenated aliphatic and aromatic hydrocarbons can also be accomplished efficiently, especially over Fe and Ni containing catalysts which serve the further function of removing the halogen from the reaction mixture by coordinating with it. Although the product distributions obtained in previous microwave catalytic studies of methane to C2 and higher hydrocarbon synthesis, and methane oxidations using water, suggested the intermediacy of radical species in the reactions, it was first demonstrated unequivocally in this work that radical intermediates are formed at the catlayst surface. The stable triphenylmethyl radical formed by the microwave induced dehalogenation of triphenylmethyl chloride or bromide was identified by esr spectroscopy.

Further work especially on the applications of this technology to the problems of decomposition of polyaromatic hydrocarbons and removal of CO_2 has yet to be done. Some

interesting early results in the reactions of CO_2 and water indicate that a variety of hydrocarbon products can be produced including methane, acetone, methanol and C3 and C4 alcohols; by recycling concentrated CO_2 emissions from sources such as coal-fired thermoelectric generating plants this may provide a method not only for diminishing the amount of this greenhouse gas emitted to the environment but also provide useful alternative fuel or chemical feedstocks.

Obviously, microwave induced catalysis can provide a flexible, efficient and fairly simple approach to many environmental problems. An increased understanding of the complex chemical interactions occurring at the catalyst surface and of the interactions of microwave energy with heterogenous materials is an essential initial stage in moving this technology from the laboratory to the marketplace.

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